

URANIUM TRANSFORMATIONS IN CONTAMINATED SEDIMENTS

Jiamin Wan, Tetsu K. Tokunaga, Terry Hazen, Mary Firestone¹, Zuoping Zheng, Jasquelin Pena, Joern Larsen, and Eoin Brodie¹

¹University of California, Berkeley

Contact: Jiamin Wan, 510/486-6004, jmw@lbl.gov

RESEARCH OBJECTIVES

Biogeochemical heterogeneity in the subsurface occurs because of transport limitations at many length scales. The question arises, when micro-environmental conditions vary significantly at the millimeter scale, where do specific biogeochemical processes occur, and how are they coupled? Within much of the subsurface, the spectrum of micro-environments is coupled through diffusive mass transfer. Thus, diffusion-limited domains are the simplest systems within which the full range of transformations can occur. Furthermore, such systems cannot be understood through characterization of bulk, volume-averaged properties because key gradients in chemical components and microbial communities are overlooked. In this research, we are investigating the biogeochemistry of uranium (U) and nitrate (NO_3^-) in diffusion-limited domains in order to understand the integrated effects of transport and biogeochemical reactions on transformations of these contaminants. Uranium and NO_3^- often occur as co-contaminants, and the reduction of soluble U(VI) to insoluble U(IV) in sediments is being considered as a strategy for *in situ* remediation. Pathways for U reoxidation need to be understood for us to critically evaluate reductive *in situ* remediation strategies. Our studies address three main segments of the subsurface U contamination cycle: (1) transport (sorption-release, diffusion, advection), (2) biogeochemistry of reduction (as influenced by NO_3^-), and (3) reoxidation.

APPROACH

Many studies are being conducted to evaluate both the individual aspects and integrated effects of the U cycle in contaminated sediments. Individual components under investigation include U(VI) sorption and release in batch systems, nitrate and U(VI) reduction in batch systems, and U(IV) reoxidation to U(VI). Column studies permit assessment of sorption-release and reduction-oxidation on overall U and NO_3^- transport. Experiments are also being done on historically contaminated and pristine soils from the NABIR Field Research Center at Oak Ridge, Tennessee.

ACCOMPLISHMENTS

The importance of calcite in suppressing U(VI) sorption into soils has been predicted and demonstrated (Zheng et al., 2003). Overall bacteria diversity in historically U-contaminated soils appeared to increase in response to lactate and NO_3^- additions, although the high diversity in *nirS* genes decreased. Lactate infusion into U-contaminated soils resulted in reduction to U(IV) within 30 days and was well reflected in redox potential measurements.

SIGNIFICANCE OF FINDINGS

The effect of calcite on suppressing U(VI) sorption was previously overlooked when standard experimental procedures were applied to slightly calcareous sediments. The sorption envelopes help explain the transient U(VI) diffusion measurements obtained in a related BES-supported study.

RELATED PUBLICATIONS

Tokunaga, T.K., J. Wan, T.C. Hazen, E. Schwartz, M.K. Firestone, S.R. Sutton, M. Newville, K.R. Olson, A. Lanzirrotti, and W. Rao, Distribution of chromium contamination and microbial activity in soil aggregates. *J. Environ. Qual.*, 32, 541–549, 2003.

Zheng, Z., T.K. Tokunaga, and J. Wan, Influence of calcium carbonate on sorption of U(VI) to soils, *Environ. Sci. Technol.*, 2003 (submitted).

ACKNOWLEDGMENTS

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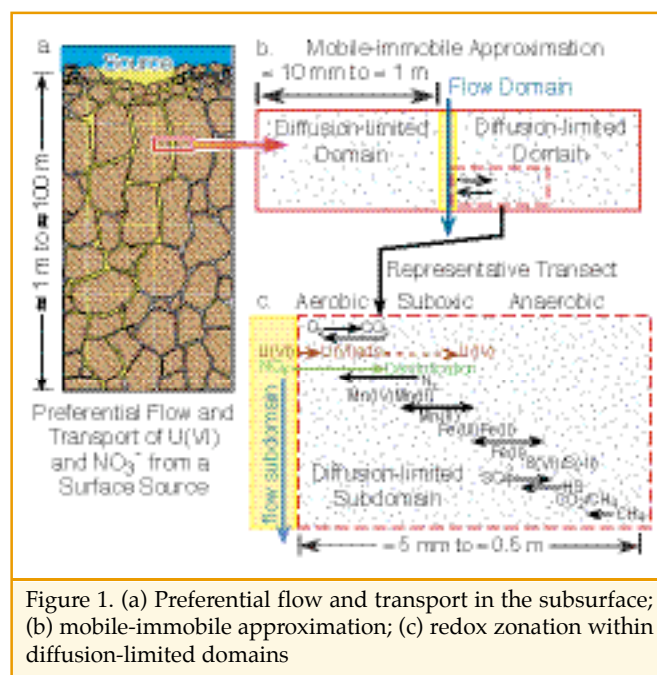


Figure 1. (a) Preferential flow and transport in the subsurface; (b) mobile-immobile approximation; (c) redox zonation within diffusion-limited domains